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Title of the Invention: METHOD FOR PRODUCING COATED DECORA-

TIVE LAMINATE

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Inventors: Kazumasa SAEGUSA, et al.
Applicant: Dai Nippon Toryo Co., Ltd.

Specification

- Title of the Invention
 Method for producing a coated decorative laminate
- 2. Claims
- (1) A method for producing a painted decorative laminate, wherein:

a ceramic substrate is coated with an undercoat cementcontaining paint consisting of an acrylic emulsion resin, an epoxy emulsion resin and a curing agent therefor, cement and a filler; and dried, and

the resultant member is coated with a topcoat paint consisting of a main component and a polyisocyanate curing component, the main component consisting of an acrylic polyol resin and a silicone resin; and dried.

- (2) A method for producing a painted decorative laminate according to claim (1), wherein the undercoat cement-containing paint consists of (A) 100 parts by weight of a mixture and (B) 30 to 300 parts by weight of water, the mixture consisting of:
- (i) 5 to 40% by weight of solid component of acrylic or methacrylic ester-copolymerized acrylic emulsion resin;

- (ii) 1 to 10% by weight of solid component of bisphenoltype epoxy emulsion resin and a curing agent therefor;
 - (iii) 20 to 60% by weight of cement; and
 - (iv) 10 to 70% by weight of the filler.
- (3) A method for producing a coated decorative laminate according to claim (1), wherein the mixture weight ratio of the acrylic polyol resin and the silicon resin in the main component of the topcoat paint is 55:45 to 85:15.
- (4) A method for producing a coated decorative laminate according to claim (1), wherein the acrylic polyol resin is a copolymer consisting of:
- (a) 1 to 45% by weight of a monoethylenically unsaturated monomer having a hydroxyl group;
- (b) 0.1 to 10% by weight of monoethylenically unsaturated carboxylic acid monomer; and
- (c) the remaining amount of other copolymerizable unsaturated monomer.
- 3. Detailed Description of the Invention
 [Field of the Invention]

The present invention relates to a method for producing a coated decorative laminate which is superior in long-time weather resistance.

[Prior Art]

Coated decorative laminates including ceramic substrates such as cement or the like coated with various paints such as an acrylic emulsion resin paint, a cement-containing acrylic emulsion paint, an acrylic resin paint, and a urethane resin paint are in wide use for the exterior of buildings and roofs, for the purpose of improvement in the appearance and protection.

[Problems to be Solved by the Invention]

In this field, as the life of buildings is extended, the above-described substrates are demanded to be finished to have a higher durability. The above-mentioned conventional paints do not provide satisfactory weather resistant, adhesiveness or the like, and require the substrates to be repainted every three to five years. Thus, the above-mentioned demand is not fulfilled.

Fluorine resin-based paints having a superior long-time weather resistance are now the subject of the target as materials for satisfying the needs of the market. However, the fluorine resin-based paints are inferior in gloss and thus cannot provide a satisfactory commercial value in this field in which the initial external appearance is taken seriously. Therefore, immediate development of coated decorative laminates which are satisfactory in the long-time weather resistance, adhesiveness, gloss and the like has been demanded.

[Means for Solving the Problems]

Under the circumstances, the present inventors performed active research to solve the above-mentioned problems and as a result, reached the present invention.

The present invention relates to a method for producing a painted decorative laminate, wherein a ceramic substrate is coated with an undercoat cement-containing paint consisting of an acrylic emulsion resin, an epoxy emulsion resin and a curing agent therefor, cement and a filler; and dried; and the resultant member is coated with a topcoat paint consisting of a main component and a polyisocyanate curing component, the main component consisting of an acrylic polyol resin and a silicone resin; and dried.

According to the method of the present invention, a composite material including an organic substance and an inorganic substance at a-specific ratio is used as the undercoat Therefore, an undercoat paint which provides, for example, a satisfactory adhesiveness between the substrate and the overcoat film, alkali resistance, and the like is obtained. The undercoat paint can be provided as a thick film and thus has an effect of alleviating the influence of thermal changes and moisture-caused size changes of the substrate on the topcoat film. The topcoat paint, which is formed of a silicone resin-modified acrylic urethane resin paint, has satisfactory gloss, weather resistance and the like. By the synergistic effect of the undercoat paint film and the topcoat paint film, the resultant film is satisfactory in the external appearance, long-time weather resistance and durability.

Hereinafter, the present invention will be described in detail.

The substrates used in the present invention are, for example, ceramic plates such as slate panels, wooden cement panels, asbestos cement panels, concrete foam plates, glass fiber-reinforced cement plates, calcium silicate plates, magnesium carbonate plates and the like used for the exterior of buildings, roofs and the like. For these substrates, flat plates or surface-processed convex-concave plates can be used as necessary.

The undercoat cement-containing paint used in the present invention includes an acrylic emulsion resin, an epoxy emulsion resin and a curing agent therefor, cement and a filler as indispensable components. Specifically, undercoat cement-containing paints consisting of the following components at the following ratios are preferable.

- (A) 100 parts by weight of a mixture consisting of:
- (i) 5 to 40% by weight of solid component of acrylic or methacrylic ester-copolymerized acrylic emulsion resin;
- (ii) 1 to 10% by weight of solid component of bisphenol-type epoxy emulsion resin and a curing agent therefor:
 - (iii) 20 to 60% by weight of cement; and
 - (iv) 10 to 70% by weight of the filler; and
 - (B) 30 to 300 parts by weight of water.

Component (i), i.e., acrylic emulsion resin is an acrylic or methacrylic ester-copolymerized emulsion resin. resentatively usable as the alkylester of the alkylester monomer having a carbon number of 1 through 8 of the acrylic acid is a component of the emulsion resin or the alkylester of the alkylester monomer having a carbon number of 1 through 8 of the methacrylic acid which is a component of the emulsion resin are, for example, methyl, ethyl, n-butyl, isobutyl, tertiary butyl, 2-ethylhexyl, benzyl, propyl, isopropyl, and sec-butyl. An ester having a carbon number of 9 or greater, which generates a gel or increases the hydrophobicity of emulsion particles at the time of emulsion polymerization, is not suitable to generation of an emulsion resin to be mixed with cement. A copolymer emulsion of one of these acrylic (or methacrylic) esters and styrene is usable, but a copolymer emulsion including styrene in an amount of 30% by weight or greater is not preferable as an emulsion resin for outdoor use which is required to have du-The reason is that an emulsion paint including rability. such a copolymer emulsion has a significantly lowered weather resistance.

Especially preferable acrylic or methacrylic esters are methyl methacrylate, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate. When styrene is used, it is preferably used in an amount of 20% by weight or less. When necessary,

a functional group monomer of an acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate or the like can be copolymerized in an amount of several percent by weight.

An advantageous range of molecular weight of these acrylic emulsion resins is 50,000 to 300,000, preferably 100,000 to 200,000. The lowest temperature of the coat film is preferably 30° C or less. When the lowest temperature is more than 30° C, cracks and fissures are likely to be generated.

These resins are preferably included in the mixture (A) in a solid component of 5 to 40% by weight. When the amount of resin is excessively small, the concentration thereof in the paint composition is excessively low. Accordingly, the surface of the coat film is formed of a resin floating due to the specific gravity difference between the filler and the cement, and is porous and is insufficient in density. As a result, efflorescence is likely to occur. In addition, since the amount of the resin component is not sufficient and thus is not sufficiently flexible, cracks and delamination are likely to occur in the coat film after a long period of time. In the case where the topcoat paint is provided thereon, an excessive long time period until the provision of the topcoat paint allows the free alkaline component in the cement to react with carbon dioxide in the air. The resultant oxide lowers the adhesiveness of the undercoat with the topcoat. When the amount of resin is excessively large, the cement and the resin are not cured sufficiently fast. Thus, a sufficient strength of the coat film is not obtained and the water resistance of the coat film is lowered.

Preferable bisphenol-type epoxy emulsion resin (component (ii)) in the undercoat cement-containing paint composition are aromatic diglycidyl ethers which are obtained from bisphenol A and epichlorhydrin and are prepared by making

resins having an average molecular weight of 350 to 1,000 water-dispersable using an emulsifier.

Examples of the epoxy resin curing agents in the paint composition are aliphatic polyvalent amines such as polyamide resin, ethylenediamine, triethylene tetramine and the like obtained by polycondensation of (i) diamine, diamine derivative or the like and (ii) dibasic acid, dibasic acid derivative or the like; and modified aliphatic polyvalent amines modified with a phenol resin, an epoxy resin or the like. The amount of the curing agent preferably corresponds to an equivalent weight of 0.8 to 1.2 of the epoxy group of the epoxy resin.

The bisphenol-type epoxy emulsion resins and curing agents therefor are preferably used in a solid component of 1 to 10% by weight in the mixture (A). When the amount of the resin is excessively small, the adhesiveness with the substrate is lowered; and when the amount of the resin is excessively large, the weather resistance of the resultant coat film is lowered.

Examples of the cement (component (iii)) in the undercoat cement-containing paint composition include portland cement, slag cement, silica cement, alumina cement, and heat-curable cement which includes portland cement as a main component and also includes a small amount of alumina cement, anhydrous plaster and/or half-hydrous plaster, and an alkaline metal salt of an organic carboxylic acid and is dried at 40 to 130°C. The cement is, however, not limited to any particular type of cement.

The cement (component (iii)) is preferably included in the mixture (A) at a ratio of 20 to 60% by weight. When the amount of the cement (component (iii)) is excessively small, the hardness of the coat film is not sufficiently improved.

When the amount of the cement (component (iii)) is excessively large, a dense and hard coat film is not obtained. As a result, the coat film is likely to cause efflorescence to occur and thus is brittle.

Examples of the filler (component (iv)) in the undercoat cement-containing paint composition include inorganic powders such as calcium carbonate, barium sulfate, magnesium carbonate, talc, clay and the like as an extender, and silica sand and the like as a aggregate. The filler is included in order to reduce the brittleness, increase the amount, and cause the above-mentioned resin component to float to the surface of the coat film by the specific gravity difference while the composition retains the fluidity after coating. For example, a filler having a large specific gravity and a grain size of 10 to 500 μm is used. The filler is preferably included in the mixture (A) at a ratio of 10 to 70% by weight, since the filler in this range provides a significant effect of causing the resin component to float and improving the properties regarding the density, brittleness, durability and the like.

The undercoat cement-containing paint can further include various color pigments and various additives such as dispersant, antifoaming agent, anti-mildew agent, film-forming agent and the like when necessary.

The undercoat cement-containing paint composition is obtained by mixing 100 parts by weight of the above-mentioned mixture (A) and 30 to 300 parts by weight of water (B) so as to have a viscosity of about 5 to 1000 poise, since in this range, the paint is easily cured and have a satisfactory operability.

The present inventors also studied on emulsion resins representatively used in the field, including vinyl acetate-

based emulsion resins such as vinyl acetate resin, vinyl acetate-acrylic resin, ethylene-vinyl acetate resin; and styrene-butadiene-based emulsion resins. The former, for example, are inferior in the weather resistance and alkaline resistance and lack long-time durability. The latter are inferior in the weather resistance and the like. Thus, these emulsion resins have been found not to be suitable for the present invention.

The topcoat paint used in the present invention includes a main component consisting of an acrylic polyol resin and a silicone resin, and a polyisocyanate curing agent as indispensable components. Specifically, topcoat paints consisting of the following components at the following ratios are preferable.

The acrylic polyol resin which is included in the main component is a copolymer having a number average molecular weight of about 2,000 to 10,000 consisting of:

- (a) 1 to 45% by weight of a monoethylenically unsaturated monomer having a hydroxyl group;
- (b) 0.1 to 10% by weight of monoethylenically unsaturated carboxylic acid monomer; and

the remaining amount of other copolymerizable unsaturated monomer.

Examples of component (a), i.e., the monoethylenically unsaturated monomer having a hydroxyl group includes hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypentyl acrylate; and methacrylic esters which is similar to the above-mentioned acrylates, n-methylolacrylamide, n-methylolmethacrylamide, and the like. A suitable amount thereof is 1 to 45% by weight. When the amount of component (a) is excessively small, the crosslinking density is insufficient and thus the properties that the resins original have are not exhibited. When the amount of

component (a) is excessively large, the polyisocyanate curing agent is required in a large amount and the resultant topcoat is usable for only a shortened period of time.

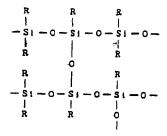
Examples of component (b), i.e., the monoethylenically unsaturated carboxylic acid monomer include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, maleic acid and anhydrides thereof. A suitable amount thereof is 0.1 to 10% by weight. When the amount of component (b) is excessively small, the speed of curing reaction of the coat film is lowered; and when the amount of component (b) is excessively large, the resultant topcoat is usable for only a shortened period of time.

Examples of component (c), i.e., the other copolymerizable unsaturated monomer include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate; unsaturated alkylester carboxylate having an alkyl group having a carbon number of 1 through 18 such as methacrylic esters similar to the above-mentioned acrylates; styrene; styrene derivatives such as vinyl toluene and the like; acrylonitrile; vinyl chloride, and the like.

The silicone resin included in the main component is, for example, an oil-like or resin-like organic siloxane condensate having a number average molecular weight of about 1,000 to 10,000 expressed by general formulas:

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or



(where R is H, methyl group or phenyl group; and R' is similar to R or -OH, -COOH, -(CH_2)_m NH_2 , (CH_2)mSR).

The main component includes an acrylic polyol resin and a silicone resin as indispensable components, and a suitable mixture weight ratio thereof is 55:45 to 85:15. When the amount of the acrylic polyol resin is smaller than the above-mentioned range, the topcoat paint has a significantly reduced gloss and is dried very slowly. Due to the slow drying, blocking is likely to occur when the coated decorative laminates are laminated, which causes problems in the coating operability. When the amount of the acrylic polyol resin is excessively large, the relative amount of the silicone resin is reduced and thus the flexibility, weather resistance and the like tend to be deteriorated.

The main component includes, when necessary, generally used organic solvents for paints, such as toluene, xylene, methylisobutylketone, methyl acetate, ethyl acetate and the like; color inorganic or organic pigments such as titanium oxide, carbon black, iron oxide red, phthalocyanine and the like; extenders such as baryte, barium sulfate, calcium carbonate, talc and the like; metal pigments such as aluminum powder, gold powder, copper powder, pearl, and the like; and various other additives for paints.

Examples of the polyisocyanate curing agent included in the topcoat paint include polyisocyanates such as hexamethylene diisocyanate, tolylene diisocyanate, xylylene di-

isocyanate, isophorone diisocyanate, lysine diisocyanate, diphenyl methane diisocyanate, cyclohexyl methane diisocyanate, nate, buret of hexamethylene diisocyanate, trimer of isophorone diisocyanate including an isocyanurate group; and compounds which are generated by reaction of these polyisocyanates and polyhydric alcohols such as propanediol, butanediol, hexanediol, polyethylene glycol, trimethylolpropane, pentaerythritol and the like, and have one or more isocyanate groups remaining therein. In terms of toxicity, drying property, and weather resistance, polymerized derivatives of hexamethylene diisocyanate, isophorone diisocyanate or lysine diisocyanate are preferable.

The mixture ratio of the main component and the curing agent included in the topcoat used in the present invention allows the equivalent weight ratio of the isocyanate group in the hydroxyl group curing agent in the main component (OH/NCO) to be 0.6 to 1.2/1. In this range, the properties which the resins originally have can be exhibited.

Next, a method for coating according to the present invention will be described.

First, a surface of the substrate is coated with an undercoat cement-containing paint prepared to have a viscosity of 15 to 80 seconds (ford cup No. 4/20°C) so as to obtain a thickness of about 0.1 to 5 mm after drying. Usable coating means are air spray, airless spray, curtain coater, airknife coater, electrostatic spray and the like. The undercoat film can be dried by forcibly drying at room temperature or a temperature of 120°C or less or, under some circumstances, vapor curing or the like.

After the substrate is coated with the undercoat paint, the resultant laminate is coated with a topcoat paint so as to obtain a thickness of about 20 to 200 μm after drying af-

ter adjusted to have a viscosity of 15 to 70 seconds (ford cup No. 4/20°C). Usable coating means are air spray, airless spray, curtain coater, roll coater, electrostatic spray and the like. The topcoat film is forcibly dried at room temperature or a temperature of 120°C or less.

[Effect of the Invention]

According to a method of the present invention, a composite material including an organic substance and an inorganic substance at a specific ratio is used as the undercoat paint. Therefore, an undercoat paint which provides, for example, a satisfactory adhesiveness between the substrate and the topcoat film, alkali resistance, and the like can be obtained. The undercoat paint can be provided as a thick film and thus has an effect of alleviating the influence of thermal changes and size changes of the substrate on the topcoat film. The topcoat paint, which is formed of a silicone resin-modified acrylic urethane resin paint, has satisfactory gloss and weather resistance. As a result, a coated decorative laminate which significantly reduces the frequency of re-painting and is satisfactory in the long-time weather resistance, durability and the like can be obtained.

Hereinafter, the present invention will be described in more detail by way of examples. In the examples, "parts" and "%" refer to parts by weight and % by weight.

The paints used in the examples and comparative examples were as follows.

<Paint A>

Solid component of acrylic emulsion resin¹⁾ 7 parts

Solid component of bisphenol-type epoxy emulsion resin (average molecular weight: 600) 3 parts

Epoxy resin modified aliphatic polyvalent amine curing agent

Portland cement48 parts

Barium sulfate	24 parts
Silica sand	13 parts
Additives	, 1 parts
Water	32 parts

Note 1) Copolymer having an average molecular weight of 150,000 consisting of methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, and styrene at 2.5:2.0:2.0:0.5.

<Paint B>

Solid component of acrylic emulsion $resin^{2}$ 20 parts Solid component of bisphenol-type epoxy emulsion resin

	2 parts
Polyamide resin curing agent	2 parts
Cement composition ³⁾	30 parts
Calcium carbonate	22 parts
Silica sand	23 parts
Additives	1 part
Vater	120 parts

Note 2) Copolymer having an average molecular weight of 140,000 consisting of methyl methacrylate, 2-ethylhexyl acrylate, and styrene at 10:7:3.

Note 3) Mixture consisting of portland cement, alumina cement, anhydride plaster, and sodium malate at 26:2.5:1:0.5.

<Paint C>

Acrylic resin solution ⁴⁾	51 parts
Silicone resin varnish ⁵⁾	16 parts
Titanium oxide	16 parts
Xylol	9 parts
Methylisobutylketone	6 parts
Polyisocyanate curing agent ⁶⁾	8 parts

Note 4) 50% toluene solution of copolymer having an average molecular weight of 6,500 consisting of styrene, methyl methacrylate, β -hydroxyethyl methacrylate, and methacrylic acid at 38:40:20:2.

Note 5) "Silicone KR216" (trade name of the product produced by Shin'etsu Silicone; xylene solution having a solid component of 70%)

Note 6) Hexamethylene diisocyanate-based polyisocyanate ("Sumijule N75", trade name of the product produced by Sumitomo Chemical Co., Ltd.)

<Paint D>

Acrylic resin solution ⁷⁾	55	parts
Silicone resin varnish ⁸⁾	14	parts
Titanium oxide	16	parts
Xylol	9	parts
Methylisobutylketone	6	parts
Polyisocyanate curing agent ⁶⁾	7	parts

Note 7) 50% toluene solution of copolymer having an average molecular weight of 4,800 consisting of styrene, ethyl methacrylate, β -hydroxyethyl methacrylate, and acrylic acid at 49.5:38:12:0.5.

Note 8) "Silicone KR214" (trade name of the product produced by Shin'etsu Silicone; xylene solution having a solid component of 70%)

<Paint E>

Acrylic resin solution ⁴⁾	31	parts
Titanium oxide	16	parts
Xylol	1	part
Methylisobutylketone	2	parts
Polyisocyanate curing agent ⁶⁾	13	parts

<Paint F>

Acrylic resin emulsion ⁹⁾	62 parts
Titanium oxide	27.5 parts
Ethylene glycol	5 parts
Ammonia water	1 part
Additives ¹⁰⁾	5.6 parts

Note 9) Copolymer emulsion having an average molecular weight of 120,000 consisting of styrene, ethyl acrylate, and butyl acrylate at 3:3:4 (solid component: 50%)

Note 10) Mixture consisting of film formation assisting agent, thickening agent, dispersant, moisture-preserving agent, anti-foaming agent, and preservative at 4.5:0.3:0.2:0.2:0.2:0.2.

Examples 1 through 3 and comparative examples 1 through 4
Surfaces of 6 mm thick slate panels were coated with undercoat paints and topcoat paints at conditions shown in Table 1 by airless spraying, and the resultant coat films were subjected to various tests. The results are shown in Table 2. In the tables, the thickness refers to the thickness in a dry state.

(seconds i ford cup No. 4/20°C) Table 1 Undercoat paint Comparative Examples examples 2 T • E Type of paint 22 مد دد 25 25 25 Viscosity of wat film 103 24 26 26 105 105 103 Thickness (um) 100×20 /20×/5 /20x20 100×10 Drying condition (°Cxmin) 120×20 / 10×10 /20×20 C D c Type of paint Viscosity of coat film 22 دد 24 26 24 26 11 26 24 Thickness (um) 100×20 /00×10 100×20 100×20 100×20 120×15 100×20 Drying condition

Table 2

	Examples			Comparative examples			
Test item	,	2	3	1	2	3	4
Initial gloss 11)	. 91	9/	9/	84	8.8	83	73
Adhesiveness (1)	100/100	100/100	100/100	100/100	100/100	98/100	90/100
Weather Gloss retaining	73	74	67	21	56	19	48
resistance Colon difference lot	1.21	1.22	1.3#	2.02	1.45	2.20	2./5

- 11) Reflectance on 60 degree mirror surface
- 12) Peeling test by cellophane tape to 1 mm grids
- 13) Gloss retaining ratio(%) and color difference after exposure for 2000 hours by Sunshine weatherometer

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